Energy levels of semiconductor surface vacancies

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We present calculations of the bound state energy levels of anion vacancies near the surface of a III–V semiconductor. We consider the (110) surface of GaAs, InP, and the Ga$_{1-x}$Al$_x$As alloy system. As the vacancy is moved toward the surface, the energy levels are only slightly perturbed until the vacancy reaches the second atomic layer from the surface. At this point, the anion vacancy levels move to lower energy. We find that there is a general trend in the vacancy energy levels with semiconductor ionicity. As the material becomes more ionic, the anion vacancy levels move to higher energy. Comparing this trend with experimentally observed Schottky barrier heights, we find a strong correlation between the position of the highest occupied level in the anion vacancy and the measured Fermi level at the surface. This result suggests that the recently proposed defect model is capable of accounting for observed trends in Schottky barrier formation.

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I. INTRODUCTION

It has recently been proposed that defects near the semiconductor surface determine the Schottky barrier height in III–V semiconductors. In this model, these defects induce localized electronic states whose energies lie in the semiconductor band gap. These states then pin the Fermi level at the energy of the defect level. Motivated by this proposal, we investigate the energy levels of a simple vacancy near the surface of a III–V semiconductor. Because anion material is found to be preferentially lost at the surface in several III–V semiconductors, we concentrate on anion vacancies. In III–V semiconductors of varying ionicity, we consider three charge states of the anion vacancy: 0, +, and −. We compute the vacancy energy level as a function of distance from the surface. We consider the position of the vacancy levels in III–V semiconductors of varying ionicity.

The paper is organized in the following way: in Sec. II, we discuss qualitatively the bound state energy levels of anion vacancy in a III–V semiconductor and the influence such vacancies would have on the surface Fermi level; in Sec. III we present our numerical results; our conclusions are contained in Sec. IV.

II. ANION VACANCIES IN III–V SEMICONDUCTORS

In the bulk of a III–V semiconductor, an ideal anion vacancy (no lattice relaxation) induces twofold and sixfold degenerate levels (including spin) with symmetry $a_1$ and $t_2$, respectively. The $a_1$ state occurs at lower energy than the $t_2$ state. There are three electrons associated with these bound (or resonant) levels in the neutral anion vacancy. Because the $t_2$ level is partially occupied (one electron) in the neutral vacancy, a Jahn–Teller distortion will occur. In Si, the vacancy with three electrons associated with the $a_2$ and $t_2$ states (positively charged in Si) is known to undergo a tetragonal Jahn–Teller distortion. We assume that the distortion for the anion vacancy in the III–V semiconductors is also tetragonal. In this case, the symmetry of the electronic states is reduced from $T_d$ to $D_{2d}$ and the $t_2$ level splits into a twofold degenerate $b_2$ level and a fourfold degenerate $e$ level. The distortion is such that the $b_2$ level is at lower energy.

We consider three charge states of the anion vacancy $V^+$, $V^0$ and $V^-$ with two, three and four electrons associated with the bound (or resonant) states, respectively. We describe the enegries of these states in analogy with the vacancy in Si. The zero energy is taken to be the $V^+$ state with no tetragonal distortion and with the electrons which will bind to form the other charge states at the Fermi energy. The energies of the three states of interest can then be written as

$$E_+ = \frac{1}{2}kQ^2, \quad E_0 = \frac{1}{2}kQ^2 + \epsilon - VQ - \mu,$$

$$E_- = \frac{1}{2}kQ^2 + 2(\epsilon - \mu - VQ) + u.$$

Here $Q$ is the displacement of a single atom in the tetragonal distortion, $k$ is the lattice restoring force constant for the displacement, $\epsilon$ is the one-electron energy (relative to the band maximum) of the $t_2$ state of the neutral vacancy with no lattice distortion, $V$ is the Jahn–Teller coupling coefficient for the distortion, $u$ is the electrostatic repulsion for the negatively charged vacancy and $\mu$ is the electron chemical potential. Physically, $Q$ is fixed for each state to minimize the energy for that state. The minimum values for the energy are:

$$E_+ = 0, \quad E_0 = \epsilon - \mu - V^0,$$

$$E_- = 2(\epsilon - \mu) - 2V^2/k + u.$$

For fixed $\mu$, the charge state of the vacancy is determined by the least of $E_+$, $E_0$, $E_-$. As pointed out in Ref. 9, there is no value of $\mu$ for which the $V^0$ state is stable if $u < V^0/k$. For this condition, $V^+$ is stable if $\mu < \epsilon - V^0/k + u/2$ and the $V^-$ is stable otherwise. If $u > V^2/k$, the neutral state may be stable. Under this condition, the $V^+$ is stable if $\mu < \epsilon - V^2/k$, $V^0$ if $\epsilon - V^2/k < \mu < \epsilon + u - 3V^2/k$, and $V^-$ if $\mu > \epsilon + u - 3V^2/k$.

In the bulk, the chemical potential is fixed by shallow dopants. However, in the defect model for Schottky barrier
formation, it is assumed that there is a large concentration of defects in a thin layer near the semiconductor surface. In this case, the position of the Fermi level relative to the band edges at the surface will be determined by the defects. For the case of a free surface (without a macroscopic metal overlayer) the defects near the surface will charge so as to compensate the charge in the depletion region of the semiconductor. From electrostatics, the Fermi level measured relative to the valence band maximum at the surface, \( \mu_s \), in n-type material is given by

\[
\mu_s = \epsilon - \frac{2\pi e^2}{\epsilon_0} \left( N_+ - N_- \right)^2 / n_d
\]

(3a)

where

\[
(N_+ - N_-) = N_r \left[ \frac{e^{E_+/kT} - e^{E_-/kT}}{e^{E_+/kT} + e^{E_0/kT} + e^{-E_-/kT}} \right].
\]

(3b)

Here \( n_d \) is the donor concentration, \( \epsilon_0 \) is the semiconductor dielectric constant and \( N_+, N_- \) and \( N_r \) are the number per unit area of positively charged, negatively charged and all vacancies, respectively. The vacancy energies are given in Eq. (2), with the one electron energy \( \epsilon \) is measured relative to the surface band edges. In p-type material, \( n_d \) in Eq. (3a) is replaced with \(- n_d\).

For a Schottky barrier with a macroscopic metal overlayer, the defects charge and form a dipole with their image charge in the metal. The charge state of the defects need not be opposite to that in the space charge region because the metal overlayer can screen the space charge. Taking the vacancies to lie in a plane a distance \( l \) from the metal surface, \( \mu_s \), in n-type material is given by

\[
\mu_s = (I_s - \chi_{nm}) + D_l + \frac{4\pi e^2 l}{\epsilon_d} \left[ (N_+ - N_-) + n_d \chi_{dm} \right]
\]

(4)

Here \( I_s \) is the semiconductor ionization potential, \( \chi_{nm} \) is the metal work function, \( \chi_{dm} \) is the depletion length, \( D_l \) is a chemically induced dipole layer which may occur at the interface and \( \epsilon_d \) is the dielectric constant of the disordered region at the interface. In p-type material \( n_d \) in Eq. (4) is replaced with \(- n_d\).

### III. RESULTS FOR ANION VACANCY LEVELS

In order to determine \( \mu_s \), it is necessary to know the parameters \( \epsilon, V, k \) and \( u \). In this section we estimate these parameters for various III-V semiconductors. We consider materials of different ionicity and attempt to correlate the results of our calculation with measured values for \( \mu_s \). We find that \( \epsilon \), for anion vacancies, increases with semiconductor ionicity in a manner similar to the experimentally observed behavior of \( \mu_s \). The other parameters are less strongly dependent on ionicity and lead to modest shifts in the position of the stability points. For example, in the calculations of Ref. 9, the \( V^0 \) state in Si is found to be unstable and the shift in stability point \( -V^2/k + u \) is 0.21 eV. We also determine the one electron energies for anion vacancies near the \( (110) \)

#### Table I. Surface Fermi level and surface vacancy concentration to complete pinning for various conditions.

<table>
<thead>
<tr>
<th>Schottky barrier</th>
<th>P(^0) stable</th>
<th>Free surface</th>
<th>Schottky barrier</th>
<th>P(^0) unstable</th>
<th>Free surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V^- )</td>
<td>( \mu_s = \epsilon - (3V^2/2k) + u )</td>
<td>( N_r \geq \frac{n_d (\mu - \mu_s)}{2\pi e^2} )</td>
<td>( \mu_s = \epsilon - (V^2/k) + (u/2) )</td>
<td>( N_r \geq \frac{n_d (\mu - \mu_s)}{2\pi e^2} )</td>
<td></td>
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<tr>
<td>( N_r \geq (I_s - \chi_{nm} + D_l) )</td>
<td>( \mu_s \geq \frac{n_d (\mu - \mu_s)}{2\pi e^2} )</td>
<td>( \mu_s \geq (I_s - \chi_{nm} + D_l) )</td>
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<td>( \mu_s = (I_s - \chi_{nm} + D_l) )</td>
<td>( \mu_s = \mu )</td>
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<td>( \epsilon = \frac{V^2}{2k} \leq \mu_s \leq \epsilon = \frac{3V^2}{2k} + u )</td>
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<td>( N_r \geq (I_s - \chi_{nm} + D_l - \mu_s) )</td>
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occupied in the neutral vacancy. In this case, the highest occupied level in the neutral vacancy is the state of interest. It is partially filled (one electron in a twofold degenerate state) and is the state which will be involved in charging the vacancy.

Our calculations are performed in the tight binding approximation. We consider GaAs, InP, and Ga$_{1-x}$Al$_x$As. Calculational details are included in Ref. 14. Our results for GaAs and InP are shown in Fig. 1. On the fifth layer from the surface, the energy levels are essentially the same as those in the bulk surface. There are two bound (or resonant) levels; the $a_1$ level is occupied with two electrons and the higher $t_2$ level has one electron in the neutral vacancy. As the vacancy is moved toward the surface, there is no significant change in the energy levels until the vacancy reaches the second atomic layer from the surface. There the $t_2$ level splits into three nondegenerate levels and they move to lower energy. The arrow indicates the highest occupied level in the neutral vacancy. For the vacancy on the surface layer, one of the bound state levels is lost. The loss occurs because only three bonds are broken in the surface vacancy and hence only three bound states can be made. The energy levels are first significantly perturbed at the second atomic layer because there a vacancy has a nearest neighbor on the surface layer. Because of reconstruction, the hybridization of the surface cation orbitals involved in the bonding is $sp^2$ rather than $sp^3$ as in the bulk. As a result, in forming the anion vacancy on the second atomic layer from the surface, a $sp^2$ bond is broken. The dangling $sp^2$ orbital is of lower energy than the dangling $sp^3$ orbitals making up the bulk vacancy states because the $sp^2$ orbital has a larger $s$ state component. On the surface layer,

$$\text{Fifth Layer Second Layer Surface Layer}$$

Fig. 1. Energy positions, relative to the band edges, of ideal anion vacancies near the (110) surface of InP and GaAs. The bound state energy levels are essentially the same as those in the bulk until the vacancy reaches the second atomic layer from the surface. The arrows indicate the highest energy state occupied in the neutral vacancy.


![Diagram](image-url)

two $sp^2$ bonds are broken and again the bound states are at lower energy than the bulk.

Comparing the results for InP with those of GaAs, we see that the anion vacancy levels in InP are at higher energy relative to the band edges. This upward shift in the energy levels occurs because InP is more ionic than GaAs. In covalent materials, the gap between valence and conduction band states is primarily due to the splitting of bonding and antibonding states. In the more ionic materials, the valence band states are primarily anion-derived and the conduction band states are more strongly cation-derived. For the covalent case, the cation dangling bonds from the anion vacancy will appear between the bonding and antibonding states, that is, near midgap. For more ionic materials, the cation dangling bond states will move toward the cation-derived states of the conduction band. Thus the vacancy levels in GaAs occur at lower energy than the corresponding states in the more ionic InP. It is interesting to note that measured values of $\mu_4$ in III–V semiconductors show a trend similar to that calculated for the anion vacancy levels. In the series GaSb, GaAs, and InP (listed in order of increasing ionicity), $\mu_4$ is observed to increase from near the valence band maximum to near the conduction band minimum.

In Fig. 2, we show the calculated position of the highest occupied level in the neutral anion vacancy in the bulk, second atomic layer and on the (110) surface of Ga$_{1-x}$Al$_x$As as a function of alloy composition. The position of these levels, relative to the valence band maximum is an increasing function of the concentration of the more ionic AlAs. The energy of the highest occupied level in the neutral anion vacancy on the surface and second layers are quite close to each other, whereas this level on the third layer (not shown explicitly) is close to that of the bulk. This occurs because the vacancy states on the surface and second layers are made heavily from dangling bond orbitals of a surface Ga which is
SP²-hybridized whereas those in the third and deeper layers are made heavily from dangling bond orbitals on Ga atoms off the surface which are SP³ hybrids. In Fig. 2 we also show the measurements of Ref. 16 for µ⁺ in Ga₁₋ₓAlₓAs as a function of x. We note that there is a strong similarity between the calculated positions of the highest filled neutral anion level and the measured position of µ⁺.

We estimate the Jahn–Teller coupling coefficients \( V \) and the Coulomb repulsion \( u \) in the bulk using perturbation theory. The unperturbed wave-function can be written as

\[
\psi_\beta(\mathbf{r}) = \sum_{\alpha} C_{\alpha \beta}^0 (\epsilon_\beta) A_{\alpha}(\mathbf{r}),
\]

where

\[
C_{\alpha \beta}^0 (\epsilon_\beta) = \frac{G_{\alpha \beta}(\epsilon_\beta)}{|-G_{\alpha \beta}(\epsilon_\beta)|^{1/2}}.
\]

Here \( \alpha \) labels an atomic function and \( j \) gives the atomic position, \( G \) is the Green’s function, \( \epsilon_\beta \) is the energy of the unperturbed state (a \( t_2 \) state is of interest here, in this case \( \beta \) indicates a \( P \) orbital), the prime in Eq. (5b) indicates an energy derivative and \( A \) is an atomic function. The Jahn–Teller coupling coefficient is calculated from

\[
VQ = \left( \psi_\beta \left| \frac{\partial H}{\partial Q} \right| \psi_\beta \right),
\]

where \( Q \) is the tetragonal normal mode displacement. The distortion potential, \( \partial H/\partial Q \), is found by assuming that the tight binding parameters scale like the overlap of the atomic functions. For GaAs and AlAs, the tetragonal distortion coupling coefficients for the \( b \) state are 1.3 eV/Å and 0.7 eV/Å, respectively. The \( e \) states shift in the opposite direction by half those amounts. The Coulomb repulsion was estimated as

\[
u = \left( \psi_\beta(\mathbf{r}_1)\psi_\beta(\mathbf{r}_2) \right) \frac{e^2}{|\epsilon(\mathbf{r}_1)|} \left( \psi_\beta(\mathbf{r}_1)\psi_\beta(\mathbf{r}_2) \right),
\]

Hence, with Jahn–Teller distortions and Coulomb corrections included, we still see a strong similarity between the calculated position of the anion vacancy levels and the measured values for \( \mu_+ \). There is, of course, some uncertainty in the absolute energy levels but we think that the trends are significant.

**IV. CONCLUSIONS**

We presented a calculation of energy levels of anion vacancies close to the (110) surface of III–V semiconductors. We have found that energy levels are not significantly changed until the vacancy reaches the second atomic layer from the surface. As one considers more ionic III–V semiconductors, the anion vacancy levels move to higher energy relative to the valence band maximum. There is a correlation between the calculated anion vacancy levels and the measured values of \( \mu_+ \) in III–V semiconductors. This correlation will probably be maintained if one considers other defect levels formed from cation dangling bonds. This correlation suggests that the defect model is a promising model of Schottky barrier formation.

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6. V. Montgomery, A. McKinley, and R. H. Williams (to be published).
10. We neglect breathing mode distortions.
12. We neglect the term \( n_{\alpha \beta} \) in Eq. (4). This term is small.
13. We use the ionization parameter defined by E. J. Mele and J. D. Joannopoulos, Phys. Rev. B17, 1525 (1978). This parameter is based on atomic energies and can be incorporated into tight binding calculations in a natural way.
15. We define 0.1 eV as significant.